

Fungicidal active compound combination

5 The present invention relates to a novel active compound combination which comprises, on the one hand, two known oxime ether derivatives and, on the other hand, a known hydroxyethyltriazole derivative and is highly suitable for controlling phytopathogenic fungi.

10 It is already known that the oxime derivative 2-[α -{[(α -methyl-3-trifluoromethylbenzyl)imino]oxy}-o-tolyl]glyoxylic acid methyl ester O-methyl oxime has fungicidal properties (cf. EP-A-0 460 575). The activity of this substance is good; however, at low application rates it is sometimes unsatisfactory. The preparation of this compound is likewise known from EP-A-0 460 575.

15 Furthermore, it is known that the hydroxyethyltriazole derivative 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro[1,2,4]triazole-3 thione has fungicidal properties (cf. WO 96/16048). The activity of this substance is good; however, at low application rates it is sometimes unsatisfactory. The preparation of this compound is likewise known from WO 96/16048.

20 Moreover, it is known that the oxime derivative 3-[1-[2-(4-<2-chlorophenoxy>-5-fluoropyrimid-6-yloxy)phenyl]-1-(methoximino)methyl]-5,6-dihydro-1,4,2-dioxazine has fungicidal properties (cf. DE-A-196 02 095). The activity of this substance is good; however, at low application rates it is sometimes unsatisfactory. The
25 preparation of this compound is likewise known from DE-A-196 02 095.

It has now been found that the novel active compound combination comprising 2-[α -{[(α -methyl-3-trifluoromethylbenzyl)imino]oxy}-o-tolyl]glyoxylic acid methyl ester O-methyl oxime of the formula (I)

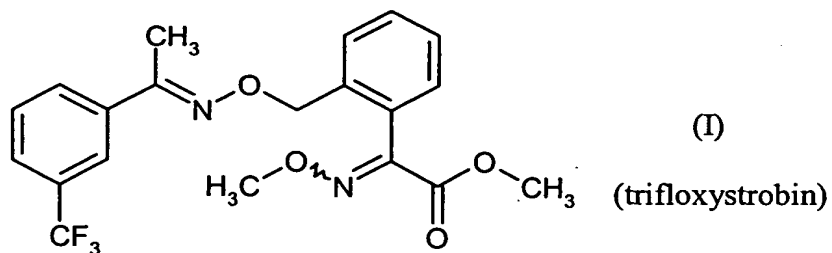
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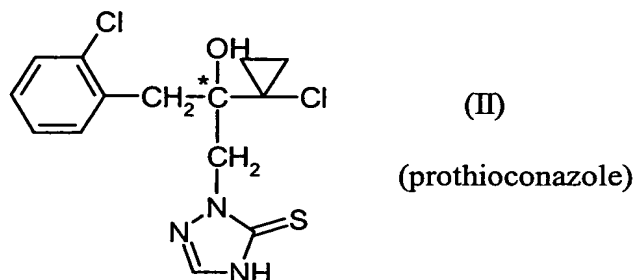
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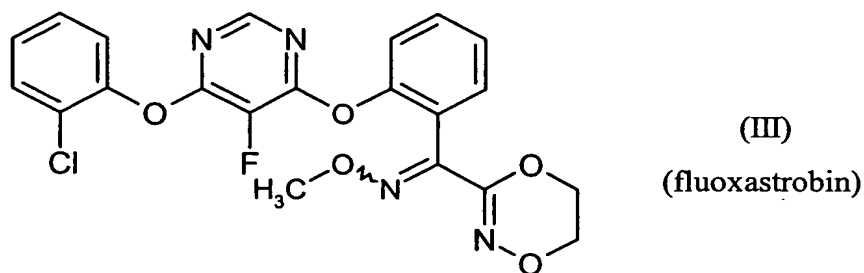
and

- 5 (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro[1,2,4]triazole-3-thione (reference: WO 96/16048) of the formula (II)



and

- 10 (2) 3-[1-[2-(4-(2-chlorophenoxy)-5-fluoropyrimidin-6-yloxy)phenyl]-1-(methoximino)methyl]-5,6-dihydro-1,4,2-dioxazine (reference: DE-A-196 02 095) of the formula (III)



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has very good fungicidal properties.

Surprisingly, the fungicidal action of the active compound combination according to the invention is considerably higher than the sum of the actions of the individual active compounds. Thus, an unforeseeable true synergistic effect is present, and not just an addition of activity.

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The active compound of the formula (I) is known (cf., for example, EP-A-460 575). The active compounds of the formulae (II) and (III) are likewise known (cf. the references cited).

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It is evident from the structural formulae of the active compounds of the formulae (I) and (III) that the compounds can be present as E or Z isomers. Accordingly, the compounds (I) and (III) can be present as a mixture of different isomers or else in the form of a single isomer. Preference is given to compounds of the formulae (I) and (III) in which the compounds of the formulae (I) and (III) are present as E isomers.

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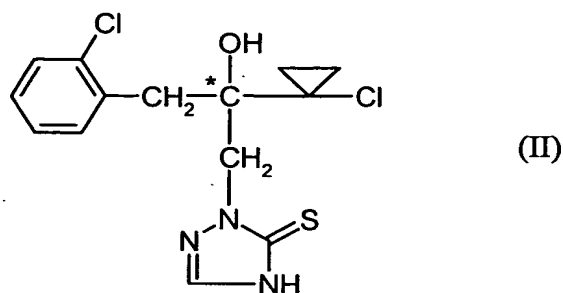
It is evident from the structural formula of the active compound of the formula (II) that the compound can be present as (-)- or as (+)-enantiomer. Accordingly, the compound (II) can be present as a racemate or else in the form of a single enantiomer. Preference is given to the compound of the formula (II) in which the racemate is present.

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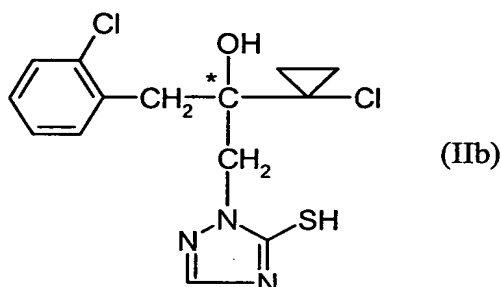
Here, the (-)-enantiomer is in each case to be understood as meaning the enantiomer which has a laevorotatory effect on the plane of vibration of linear-polarized light of the sodium D line. DE-A-199 17 617 discloses a process for preparing the (-)-enantiomer.

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The hydroxyethyltriazole derivative of the formula (II) can furthermore be present in the "thiono" form of the formula



or in the tautomeric "mercapto" form of the formula



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For the sake of simplicity, only the "thiono" form is shown in each case.

10 The active compound combination according to the invention comprises the active compounds of the formulae (I), (II) and (III). In addition, it may also comprise further fungicidally active additives.

15 If the active compounds in the active compound combinations according to the invention are present in certain weight ratios, the synergistic effect is particularly pronounced. However, the weight ratios of the active compounds in the active compound combinations can be varied within a relatively wide range.

In general,

20 from 0.1 to 10 parts by weight, preferably from 0.2 to 5 parts by weight, of active compound of the formula (II)

and

from 0.1 to 10 parts by weight, preferably from 0.2 to 5 parts by weight, of active compound of the formula (III)

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are present per part by weight of active compound of the formula (I).

The active compound combinations according to the invention have very good fungicidal properties and can be employed for controlling phytopathogenic fungi, such as Plasmodiophoromycetes, Oomycetes, Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes, Deuteromycetes, etc.

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The active compound combination according to the invention is particularly suitable for controlling cereal diseases, such as Erysiphe, Cochliobolus, Pyrenophora, Rhynchosporium, Septoria, Fusarium, Pseudocercospora and Leptosphaeria and for controlling fungal infections in non-cereal crops such as vine, fruit, groundnut, vegetables, for example Phytophthora, Plasmopara, Pythium, powdery mildew of fungi, such as, for example, Sphaerotheca or Uncinula, and causative organisms of leaf spot, such as Venturia, Alternaria and Septoria and also Rhizoctonia, Botrytis, Sclerotinia and Sclerotium.

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The fact that the active compound combinations are well tolerated by plants at the concentrations required for controlling plant diseases permits the treatment of above-ground parts of plants, of propagation stock and seeds, and of the soil. The active compound combinations according to the invention can also be employed for foliar application or else as seed dressings.

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The active compound combinations according to the invention are also suitable for increasing the harvest yield. Moreover, they have reduced toxicity and are tolerated well by plants.

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According to the invention, it is possible to treat all plants and parts of plants. Plants are to be understood here as meaning all plants and plant populations such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional breeding and optimization methods or by biotechnological and genetic engineering methods or combinations of these methods, including the transgenic plants and including the plant cultivars which can or cannot be protected by plant breeders' certificates. Parts of plants are to be understood as meaning all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stems, trunks, flowers, fruit-bodies, fruits and seeds and also roots, tubers and rhizomes. Parts of plants also include harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

The treatment of the plants and parts of plants according to the invention with the active compounds is carried out directly or by action on their environment, habitat or storage area according to customary treatment methods, for example by dipping, spraying, evaporating, atomizing, broadcasting, brushing-on and, in the case of propagation material, in particular in the case of seeds, furthermore by one- or multi-layer coating.

The active compound combinations according to the invention can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols and microencapsulations in polymeric substances and in coating compositions for seeds, and ULV formulations.

These formulations are produced in a known manner, for example by mixing the active compounds or active compound combinations with extenders, that is liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants, and/or foam formers. If the extender used is water, it is also possible to use, for example, organic solvents as

auxiliary solvents. Essentially, suitable liquid solvents include: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, or else water. Liquefied gaseous extenders or carriers are to be understood as meaning liquids which are gaseous at ambient temperature and under atmospheric pressure, for example aerosol propellants such as butane, propane, nitrogen and carbon dioxide. Suitable solid carriers are: for example ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina and silicates. Suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks. Suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, or else protein hydrolysates. Suitable dispersants are: for example lignin-sulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colourants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs such as alizarin dyestuffs,

azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

5 The formulations generally comprise between 0.1 and 95% by weight of active compounds, preferably between 0.5 and 90%.

10 The active compound combinations according to the invention, as such or in their formulations, can also be applied in a mixture with known fungicides, bactericides, acaricides, nematocides or insecticides, to broaden the activity spectrum or to prevent the development of resistance, for example. In many cases, synergistic effects are obtained, i.e. the activity of the mixture is greater than the activity of the individual components.

15 A mixture with other known active compounds such as herbicides or with fertilizers and growth regulators is also possible.

20 The active compound combinations can be used as such, in the form of their formulations or as the use forms prepared therefrom, such as ready-to-use solutions, emulsifiable concentrates, emulsions, suspensions, wettable powders, soluble powders and granules. They are used in the customary manner, for example by watering, spraying, atomizing, scattering, spreading, and as a powder for dry seed treatment, a solution for seed treatment, a water-soluble powder for seed treatment, a water-soluble powder for slurry treatment, or by encrusting.

25 When using the active compound combinations according to the invention, the application rates can be varied within a relatively wide range, depending on the kind of application. In the treatment of parts of plants, the application rates of active compound combination are generally between 0.1 and 10 000 g/ha, preferably between 10 and 1 000 g/ha. In the treatment of seeds, the application rates of active
30 compound combination are generally between 0.001 and 50 g per kilogram of seed, preferably between 0.01 and 10 g per kilogram of seed. In the treatment of the soil,

the application rates of active compound combination are generally between 0.1 and 10 000 g/ha, preferably between 1 and 5 000 g/ha.

5 The good fungicidal activity of the active compound combinations according to the invention is evident from the examples below. While the individual active compounds exhibit weaknesses with regard to fungicidal activity, the combinations have an activity which exceeds the sum of individual activities.

10 A synergistic effect in fungicides is always present when the fungicidal activity of the active compound combinations is greater than the sum of the activities of the active compounds applied individually.

The invention is illustrated by the examples below. However, the invention is not limited to the examples.

15

Example 1

Pyrenophora teres test (barley) /curative

- 5 Solvent: 25 parts by weight of N,N-dimethylacetamide
 Emulsifier: 0.6 part by weight of alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amount of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

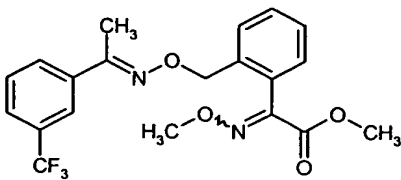
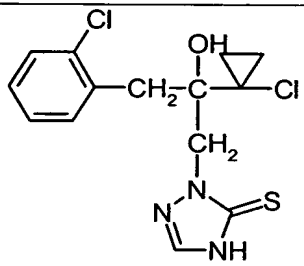
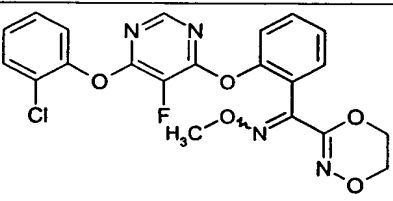
15 To test for curative activity, young plants are sprayed with a conidia suspension of *Pyrenophora teres*. The plants remain in an incubation cabin at 20°C and 100% relative atmospheric humidity for 48 hours. The plants are then sprayed with the preparation of active compound at the stated application rate.

 The plants are placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80%.

20 Evaluation is carried out 7 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Table 1

Pyrenophora teres test (barley) / curative

Active compound	Application rate of active compound in g/ha	Efficacy in %
<u>known:</u>  (I) (trifloxystrobin)	100	56
 (II) (prothioconazole)	100	56
 (III) (fluoxastrobin)	100	67
<u>Mixture according to the invention (1:2:1)</u> (I) (II) (III)	25 50 25	78